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Vol. 67. No. 1.—January, 1932.

VOLUME-TEMPERATURE-PRESSURE RELATIONS FOR SEVERAL NON-VOLATILE LIQUIDS.

By P. W. Bridgman.

Investigations on Light and Heat made and published with aid from the Rumford Fund.

(Continued from page 3 of cover.)

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Presented Oct. 14, 1931. Received Oct. 16, 1931.

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Introduction.

The material of this paper constitutes an extension to new liquids of measurements of volume as a function of pressure and temperature by the sylphon method recently developed and described.[1] The apparatus, and methods of experiment and calculation were the same as in the first paper and need not be described again in detail.

Most of the liquids of this paper were chosen particularly with a view to finding organic liquids which should be as incompressible as possible. One of the interesting results which had appeared in the previous paper on summarizing all available data for the volume of organic liquids at high pressures was the exceptionally low compressibility of glycerine, which stands in a class by itself with a compressibility about one half as great as that of water, which in its turn is of

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the order of only half as compressible as the majority of all other liquids hitherto measured. The problem that suggested itself, therefore, was to find if possible other organic liquids as incompressible as glycerine. This was interesting on its own account as throwing some light on the reasons for low compressibility in organic liquids, and also had an incidental interest in that the sylphon method of measuring compressibilities could be extended to solid substances if liquids could be found of high incompressibility with which to transmit pressure to the solids in the sylphon. Pursuant to this program, four liquids were investigated in the same chemical series as glycerine, and in addition, glycerine itself was remeasured, the previous measurements having been made at only a single temperature. These measurements showed nothing less compressible than glycerine; the measurements made evident in what direction in the series incompressibility increases, and also that glycerine is the most incompressible liquid available in the series, the next members in the direction of increasing incompressibility being solid rather than liquid. Another clue was therefore followed in the further search for incompressibility. Low compressibility might reasonably be associated with low thermal expansion, and this in its turn is known to be associated with low vapor pressure. The Eastman Kodak Co., in their search for liquids suitable for diffusion pumps, has recently issued a list of organic liquids with vapor pressures less than that of mercury. Half a dozen of these liquids, of widely varying chemical composition, were selected for measurement. These all proved to be much more incompressible than the ordinary organic liquid, but nothing was found superior to glycerine.

In addition to the eleven liquids just described and chosen with a view to high incompressibility, three other liquids were investigated for various reasons. Eugenol was measured because of the interesting effects found by W. E. Danforth, Jr.,[2] in measurements of the effect of pressure on its dielectric constant, which demanded a knowledge of volume as a function of pressure to bring out their full significance. Iso-octane which has recently become available through the activities of one of the large commercial research laboratories, was measured in order to supplement the measurements of the preceding paper on normal octane. Isoprene was measured in order to supplement the studies previously made by Professor J. B. Conant, C. O. Tongberg, and W. R. Peterson[3] on the effect of pressure in causing it to polymerize to rubber.

Details of Experiment or Calculation.

The measurements given in the following differ in only two important respects from those in the preceding paper. In the first place, a knowledge of the density of the liquid at 0° C at atmospheric pressure is necessary in order to reduce the sylphon readings to fractional changes of volume. The necessary data have been previously determined in only a few cases, so that special measurements had to be made. These usually consisted of a determination of the density at room temperature at atmospheric pressure by weighing a mass of copper immersed in the liquid. To reduce this density to 0° the thermal expansion is also necessary. This was not directly measured at atmospheric pressure, but was found by an extrapolation of the measurements under pressure of the volume at 0° and 50°. At 0° the volume was measured in the sylphon as a function of pressure down to atmospheric pressure, but at 50° the lowest pressure was usually about 200 kg/cm^2. The thermal expansions between 0° and 50° at 200, 400, 600, 800, and 1000 kg were obtained from the sylphon readings, and extrapolated back to atmospheric pressure. This could be done with very little uncertainty because the curvature was slight, and even sometimes the thermal expansion was sensibly a linear function of pressure over this range. The density at 0° was then calculated from the observed density at 25° at atmospheric pressure with the value just obtained for the thermal expansion, assuming that at atmospheric pressure the thermal expansion is linear in temperature between 0° and 50°. This again is not quite exact, but the error so introduced cannot be large.

In the following the necessary data are given so that in the future correction can be made for the various effects just discussed if it should prove necessary. The tables of volume given in the following ostensibly contain the relative volumes in terms of the volume at 0° C and atmospheric pressure as unity. The tables were actually constructed, however, in the first place by measuring the volume decrements of a certain weight of liquid, reducing these volume decrements by division to values corresponding to the weight of liquid which by calculation would occupy 1 cm^3 at 0°C at atmospheric pressure, and then finding the actual volumes by subtracting these volume decrements from 1.0000.

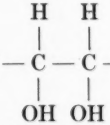
The way in which corrections should be applied in case of future improvements in the thermal expansion at atmospheric pressure may be shown by a detailed example. Consider methyl oleate. The

decrements for this are stated to be for 0.8950 gm, which means that the density at 0° C at atmospheric pressure, D_0, was taken to be 0.8950. The measured density at atmospheric pressure at 26.0° is stated to be 0.8768. The extrapolated thermal expansion must therefore have been such as to increase the density from 0.8768 at 26° to 0.8950 at 0°. The mean thermal expansion between 0° and 26° was therefore $\left(\frac{1}{.8768} - \frac{1}{.8950}\right)\frac{1}{26} = \frac{1.14051 - 1.11732}{26} = \frac{.02319}{26}$ = .000893. Suppose now that future experiment shows that a better value for the mean thermal expansion in this range is 0.00095. Then $\frac{1}{D_0}[1 + 26 \times .00095] = \frac{1}{.8768}$. (The density at 26° must not be adjusted even if future measurements on methyl oleate give a better value, because the error of measurement of the density was here low enough to give valid values, and future disagreement must be ascribed to differences in the purity of the liquid.) Solving the last equation for D_0 gives $D_0 = .8768 \times 1.02470 = .8984$. The Table should therefore have been constructed for 0.8984 gm rather than 0.8950 gm. The volume decrements in the table must therefore be multiplied by $\frac{.8984}{.8950}$. This would give, for example, a volume at 0° and 1500 kg of $\left[1.0000 - \frac{.8984}{.8950} \times .0638\right] = 1.0000 - .0640 = .9360$. Again, to get the correct volume at 95° and 1500 kg the volume difference in the table between 95° and 0° at 1500 kg (i. e. 0.9886 − 0.9362 = 0.0524) is to be multiplied by $\frac{.8984}{.8950}$ (= 0.0526), and this added to the corrected volume at 0° and 1500 kg, giving for the final volume 0.9360 + 0.0526 = 0.9886, accidentally the same as the original volume. The volume differences in the tables were constructed as far as possible on the isotherms at 0°; at pressures higher than the maximum pressure allowed at 0°, they were constructed from the maximum pressure of the 0° isotherm, which in the case of methyl oleate is 1500 kg, and the appropriate temperature as a fiducial point. Thus in the example above, the corrected volume at 95° and 10000 kg would be $.9886 - [.9886 - .8373]\frac{.8984}{.8950} = .8367$, instead of .8373.

In a second respect the experimental procedure was different from that in the preceding paper. The maximum pressures attainable are

in many cases limited by the freezing of the liquid. In the previous paper there was often sufficient data already available to allow some guess to be made at what the freezing pressures might be, but so few of the physical properties of the liquids of this paper have been tabulated that a direct determination of the freezing pressures was undertaken for some of the liquids. This usually took the form of a freezing point determination at atmospheric pressure by the method of temperature arrest, the substance being first solidified at liquid air temperature, and then the rise of temperature, as given by a thermocouple imbedded in the substance, observed as a function of time, melting being indicated in the conventional way by a flat place in the curve. The freezing under pressure was usually determined at room temperature. This was done as simply as possible. A cylinder with a hole 5/16 of an inch, 0.79 cm, in diameter was filled with the liquid, the manganin pressure gauge being directly immersed in the liquid. The liquids were in all cases good enough insulators so that this could be done with no appreciable amount of short circuiting. Pressure was then increased by pushing in the piston, and the piston position was plotted against the pressure as given by the manganin gauge. Freezing was indicated by a flat place in the curve. After the substance had been frozen by increasing pressure, readings were usually repeated with decreasing pressure, in this way getting a better value for the freezing pressure without error from subcooling. The two points, at atmospheric pressure and at room temperature, were usually good enough to give a sufficient indication of the range of pressure at any temperature that might safely be applied without runnuing into the freezing curve.

Detailed Presentation of Data.

Ethylene Glycol.  This material was obtained from the Eastman Kodak Co., and was used without further purification. In order to avoid the possibility of freezing, runs were made first at 50° and 95° to 12000 kg, starting the run at 50° at atmospheric pressure. These runs were accomplished without incident, the points with increasing and decreasing pressure lying on the same smooth curve. After the run at 95° it was necessary to take the apparatus

apart to renew some of the insulation, and on reassembling the apparatus and starting the run at 0° it was evident that some permanent distortion had been introduced into the sylphon, probably by releasing the pressure to atmospheric before the sylphon had sufficiently cooled. Furthermore, the run at 0° encountered stationary readings, indicating freezing, at about 6000 kg. This, however, was not the true freezing pressure, but was too high because of subcooling; in fact pressure was released as far as 3300 kg without signs of melting. So great a subcooling was not anticipated, and the apparatus was again dismantled for inspection, with the expectation of finding the sylphon ruined. No difficulty was obvious, however, and weighing showed that there had been no leak. The apparatus was then again reassembled, and the 0° readings checked. The run was then concluded with several readings at 50° and 95° and then back to 0°, in order to establish the temperature expansion, which could not be obtained between 50° and 95° because of the distortion on the first disassembly. This experiment provides a rather extreme example of the amount of abuse a sylphon will sometimes support without being put out of commission. The average deviation from a smooth curve of a single one of the 70 readings was 0.26% of the maximum effect, treating the readings after the distortion as belonging to a different series from those before it.

TABLE I.

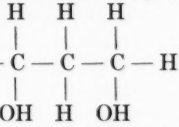
RELATIVE VOLUMES OF ETHYLENE GLYCOL.

Pressure	Temperature		
kg/cm²	0°	50°	95°
0	1.0000	1.0300	
500	.9841	1.0133	
1,000	.9703	.9979	1.0278
1,500	.9589	.9846	1.0091
2,000	.9486	.9724	.9938
3,000	.9304	.9519	.9708
4,000	.9154	.9343	.9515
5,000	.9032	.9197	.9352
6,000		.9073	.9215
7,000		.8959	.9089
8,000		.8851	.8982
9,000		.8753	.8883
10,000		.8664	.8789
11,000		.8585	.8706
12,000		.8503	.8627

The relative volumes are given in Table I. The volume decrements in the table are for 1.1263 gm. The density, as directly determined from the loss of weight of an immersed copper weight was 1.1137 at 20.25°. In reducing this to the density at 0°, 1.1263, the total thermal expansion of 1 gm of the liquid between 0° and 50° at atmospheric pressure was taken as 0.0267 cm^3, this being the value given directly by the sylphon measurements.

It is not at all improbable that the melting pressures at 50° and 95° may be below the maximum of 12000 kg reached in these measurements, the substance having remained liquid by subcooling. A similar effect is known to exist in glycerine, in which the subcooling is very marked, and it is not unreasonable to expect the same effect here.

Tri-methylene Glycol.

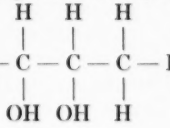


This was obtained from the Eastman Kodak Co., and was most kindly further purified by fractional distillation by Professor Conant, who did not find, however, any marked change in its boiling point introduced by the redistillation.

Runs were made at 0° to a maximum of 5000 kg, and then at 50° and 95° to 12000 kg, with no sign of freezing at any temperature. There was an unexplained break between 0° and 50°, not due to the sylphon, which was taken down and checked between the two runs; the break was probably due to an inadvertent and unrecorded change in the electrical constants of the potentiometer. The return check readings were made at 50° and 0° as usual, and the thermal expansion between 0° and 50° taken from the check readings. The average departure from smooth curves of a single one of the 61 readings was 0.28% of the maximum effect.

The relative volumes are shown in Table II. The volume decrements listed in the table are for 1.063 gm. The density at 20.2° at atmospheric pressure determined by buoyancy measurements was 1.0528. This substance is listed in International Critical Tables, for which the density at 20° is given as 1.053, very good agreement.

Propylene Glycol.



This material was ob-

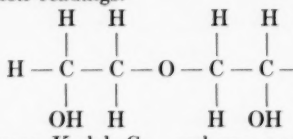
tained from the Eastman Kodak Co., and was used without further purification. Readings were made first at 0° to a maximum of 4200 kg, then at 50° to 12000, at 95° to 12000, a return check reading at 50° at 900 kg, and then the run at 0° was repeated to a maximum of 12000 and back, with perfect agreement with the first run in the common interval, and no indication of freezing at any temperature. The average departure from smooth curves of a single one of the 73 readings was 0.13% of the maximum effect.

TABLE II.

RELATIVE VOLUMES OF TRI-METHYLENE GLYCOL.

Pressure kg/cm²	Temperature 0°	50°	95°
0	1.0000	1.0274	
500	.9830	1.0082	
1,000	.9671	.9929	1.0165
1,500	.9547	.9799	1.0016
2,000	.9432	.9678	.9879
3,000	.9237	.9472	.9640
4,000	.9072	.9300	.9450
5,000	.8922	.9150	.9292
6,000		.9020	.9154
7,000		.8898	.9030
8,000		.8792	.8919
9,000		.8707	.8817
10,000		.8630	.8729
11,000		.8553	.8655
12,000		.8474	.8582

The relative volumes are given in Table III; the volume decrements are for 1.0486 gm. The measured density at 20° was 1.0340. International Critical Tables gives 1.038 at 23°, not especially good agreement. The assumed value for the density at 0°, 1.0486, was obtained by taking the total expansion at atmospheric pressure between 0° and 50° to be 0.0325 cm³, a value obtained by slight extrapolation of the sylphon readings.

Diethylene Glycol.  This was obtained from the Eastman Kodak Co., and was used without further

purification. The first run was at 0° to a maximum of 5800 kg. At this pressure a stationary reading was obtained, indicating freezing. Temperature was raised at once to 50° in order to avoid possible damage to the sylphon, but in spite of this precaution, some permanent set was produced. At 50°, pressure was lowered to 300 kg, increased back to 12000, and then lowered back to 400; all the points at 50° lay on the same smooth curve, indicating no further damage to the sylphon. The 95° run was next made, then the check reading at 50°, with perfect agreement, and finally a new curve was obtained at 0°, up to 4500 and back. The average deviation from smooth curves of a single one of the 62 readings was 0.25% of the maximum effect.

TABLE III.

RELATIVE VOLUMES OF PROPYLENE GLYCOL.

Pressure	Temperature		
kg/cm²	0°	50°	95°
0	1.0000		
500	.9819	1.0129	
1,000	.9664	.9947	1.0201
1,500	.9540	.9794	1.0027
2,000	.9432	.9659	.9877
3,000	.9237	.9454	.9637
4,000	.9070	.9266	.9430
5,000	.8935	.9120	.9257
6,000	.8809	.8989	.9110
7,000	.8679	.8864	.8985
8,000	.8569	.8750	.8867
9,000	.8472	.8652	.8763
10,000	.8380	.8563	.8672
11,000	.8294	.8477	.8589
12,000	.8219	.8400	.8514

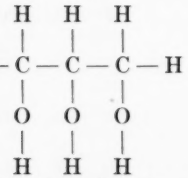
The relative volumes are given in Table IV. The density at 0° at atmospheric pressure was taken as 1.1298, which is therefore the number of grams to which the volume decrements of the table refer. The directly measured density at 25° was 1.1122. This does not agree particularly well with the value of International Critical Tables, which is 1.132 at 20°. In calculating the density at 0°, the total expansion of one gram between 0° and 25° was taken to be 0.0142 cm³, a value calculated, as explained, by a slight extrapolation of the sylphon readings at 50°.

TABLE IV.

RELATIVE VOLUMES OF DIETHYLENE GLYCOL.

Pressure kg/cm²	Temperature 0°	50°	95°
0	1.0000	1.0320	
500	.9845	1.0135	
1,000	.9710	.9987	1.0223
1,500	.9604	.9861	1.0077
2,000	.9492	.9729	.9833
3,000	.9320	.9523	.9705
4,000	.9174	.9352	.9522
5,000	.9047	.9207	.9368
6,000		.9075	.9235
7,000		.8963	.9113
8,000		.8859	.9005
9,000		.8762	.8902
10,000		.8677	.8810
11,000		.8608	.8728
12,000		.8542	.8648

Glycerine.



This was Kahlbaum's purest grade, "Zur Analyse," used without further purification. It was, however, doubtless, somewhat impure with water, as shown by the low value of the density, discussed in the next paragraph. This material had been previously measured, but only at a single temperature, and with the free piston piezometer, which is not capable of such great accuracy as the sylphon. Readings were first made at 0° to a maximum of 5000, then at 50° to 12000 and back, at 95° to 12000 and back, and then the run at 0° was repeated, this time to 12000 and back, with a perfect check on the common portions of the two 0° curves. Particular care was taken to change the pressure slowly, because the viscosity of gylcerine is known to increase greatly under pressure. The average deviation from smooth curves of a single one of the 65 readings was 0.31% of the maximum effect. Two thirds of the total irregularity was contributed by the 13 points of the 0° run above 6000 kg, and is without doubt the expected effect of viscosity.

The relative volumes are given in Table V. The density at atmospheric pressure at 0° was taken as 1.2385, and the volume decrements of the table are for this number of grams. The measured density at atmospheric pressure at 24.6° was 1.2226. International Critical Tables gives at 20° 1.260. The low value for this glycerine is to be explained by the presence of water. That this was the case was checked later by Mr. W. E. Danforth, Jr. who tried to measure the effect of pressure on the dielectric constant of this same material without success, because of its high conductivity, which means water. He was able to remove the water sufficiently for his purposes by chemical means; it might pay at some future time to redetermine the compressibility of entirely water-free glycerine. The effect of the water cannot be large, however, as may be seen by a comparison of the values of Table V with those given in the preceding paper for a 50% water-glycerine mixture.

TABLE V.

RELATIVE VOLUMES OF GLYCERINE.

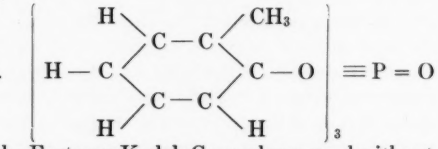
Pressure kg/cm²	Temperature 0°	50°	95°
0	1.0000	1.0266	
500	.9900	1.0136	
1,000	.9806	1.0025	1.0240
1,500	.9721	.9930	1.0125
2,000	.9641	.9843	1.0024
3,000	.9501	.9688	.9853
4,000	.9373	.9548	.9700
5,000	.9264	.9423	.9565
6,000	.9157	.9310	.9447
7,000	.9057	.9211	.9342
8,000	.8958	.9121	.9244
9,000	.8867	.9036	.9152
10,000	.8783	.8955	.9070
11,000	.8712	.8879	.8994
12,000	.8648	.8800	.8925

The density at 0° at atmospheric pressure was calculated from the measured density at 24.6° by taking 0.0215 cm³ for the total expansion between 0° and 50° of one gram, a value obtained by extrapolation of the sylphon readings at 50°.

Comparison with the previous values of the compressibility of glycerine from the same source gives rather good agreement within the

limits of error of the previous method. The former values for the relative volumes at 30° at 0, 2000, 4000, 6000, 8000, 10000, and 12000 kg respectively are: 1.000, 0.958, 0.932, 0.911, 0.893, 0.879, and 0.866. The values obtained by linear interpolation between 0° and 50° of the present measurements are: 1.000, 0.960, 0.933, 0.910, 0.891, 0.875, and 0.860. Compared with the sylphon, the former free piston seems to give volume changes which are too large at low pressures and too small at high pressures.

Tri-o-cresyl-Phosphate.



This was obtained from the Eastman Kodak Co. and was used without further purification. The first run at 0° indicated freezing somewhere between 2200 and 3000 kg. At the latter pressure temperature was raised immediately to 50°, and the run at 50° made to a maximum of 4900 kg, and then the run at 95° to a maximum of 6200. The return check reading at 0° now showed that a permanent distortion had taken place at the first freezing; the run at 0° was repeated to a maximum of 1800, giving a curve of the same shape as the first curve, but displaced by a constant amount. Points on the 50° and the 95° curve were then repeated, giving agreement with the first determinations. The average deviation from smooth curves of a single one of the 36 readings was 0.54% of the maximum effect. The greater irregularity than usual is to be explained in part by the much narrower range than usual.

TABLE VI.

RELATIVE VOLUMES OF TRI-O-CRESYL PHOSPHATE.

Pressure	Temperature		
kg/cm²	0°	50°	95°
0	1.0000	1.0302	
500	.9831	1.0109	
1,000	.9687	.9938	1.0163
1,500	.9573	.9790	.9994
2,000	.9478	.9669	.9858
3,000		.9468	.9630
4,000		.9308	.9448
5,000		.9180	.9300
6,000			.9166

The relative volumes are given in Table VI. The density at 0° at atmospheric pressure was taken to be 1.1987, which means that the volume decrements listed in the table are for this number of grams. The directly measured density was 1.1803 at 25°. The volume expansion of one gram at atmospheric pressure between 0° and 50° was taken to be 0.02528, obtained by extrapolation of the sylphon readings.

Tri-acetin. CH_3COOCH_2 | CH_3COOCH | CH_3COOCH_2 The material was obtained from the Eastman Kodak Co. and used without further purification. Runs were made at 0° to a maximum of 4900 kg, at 50° to 10000, and at 95° to 12000, with a return check reading at 0° with good agreement. The maxima at 0° and 50° were as high as it was thought safe to go in view of a preliminary freezing point examination in the special small apparatus; the indications of freezing were not very sharp, however, and it should not be assumed without further examination that the limits mentioned above are actually very close to the freezing points. The average departure from smooth curves of a single one of the 44 readings was 0.13%.

TABLE VII.

RELATIVE VOLUMES OF TRI-ACETIN.

Pressure kg/cm²	Temperature 0°	50°	95°
0	1.0000	1.0441	
500	.9793	1.0198	
1,000	.9627	.9981	1.0289
1,500	.9492	.9805	1.0071
2,000	.9374	.9653	.9893
3,000	.9177	.9412	.9628
4,000	.9012	.9225	.9432
5,000	.8861	.9068	.9258
6,000		.8932	.9098
7,000		.8807	.8956
8,000		.8694	.8831
9,000		.8591	.8721
10,000		.8498	.8624
11,000			.8533
12,000			.8445

The relative volumes are given in Table VII. The density at 0° at atmospheric pressure was taken as 1.2157, so that the volume decrements in the table are for this number of grams. The directly measured density at 26.9° was 1.1613; in reducing this to the density at 0° the expansion of one gram between 0° and 26.9° was taken to be 0.0194 cm^3, obtained by extrapolation of the sylphon readings. This substance is unusual in that the thermal expansion between 0° and 50° is linear in the pressure up to 1100 kg/cm^2 within the limits of experimental error.

Ethyl Dibenzyl Malonate. This was obtained from the Eastman Kodak Co. and used without further purification. A preliminary freezing exploration indicated that the freezing pressure was very low, and the limits of the measurements were set by this exploration. The first run was made at 50° to a maximum of 2100 kg, then at 95° to 5000, at 50° again to a maximum of 3000, at 0° to 1000, with a final check reading at 50° in perfect agreement. The average departure from smooth curves of a single one of the 31 readings was 0.48% of the maximum effect. The irregularity, which is somewhat greater than usual, is to be entirely explained by the small range, the average absolute irregularity in the readings being no greater than usual.

TABLE VIII.

RELATIVE VOLUMES OF ETHYL DIBENZYL MALONATE.

Pressure	Temperature		
kg/cm^2	0°	50°	95°
0	1.0000	1.0361	
500	.9775	1.0111	
1,000	.9620	.9912	1.0172
1,500		.9748	.9979
2,000		.9616	.9823
3,000		.9412	.9581
4,000			.9381
5,000			.9179

The relative volumes are shown in Table VIII. The density at 0° at atmospheric pressure was taken to be 1.1143, so that the volume decrements in the table refer to this number of grams. The directly measured density at 25.9° was 1.0943; the density at 0° was calculated from this, using for the total expansion of one gram between 0° and

25.9° 0.0167 cm³, a value obtained by extrapolation of the sylphon readings. The thermal expansion between 0° and 50° is again linear in the pressure up to 1000 kg.

Methyl Oleate. $CH_3(CH_2)_7CH = CH(CH_2)_7COOCH_3$. This was obtained from the Eastman Kodak Co. and used without further purification. A preliminary freezing point determination gave an unusually sharp freezing point between 2900 and 3300 kg at 24°; this may be accepted with some confidence as the proper freezing coordinate. In the compressibility measurements the range was fixed by this information, together with the freezing point at atmospheric pressure listed in tables of physical constants. Two sets of runs were made; the first was terminated by damage to the sylphon before the return check readings could be made. The second set-up with a new sylphon gave first a run at 95° to 10000 kg, one at 50° to 5900, one at 0° to 1800, and finally a return check reading at 95° with perfect agreement. The average deviation from smooth curves of a single one of the 30 readings, discarding a single one where there must have been a blunder in recording, was 0.20%.

TABLE IX.

RELATIVE VOLUMES OF METHYL OLEATE.

Pressure kg/cm²	Temperature 0°	50°	95°
0	1.0000	1.0401	
500	.9740	1.0103	
1,000	.9532	.9859	1.0110
1,500	.9362	.9669	.9886
2,000		.9509	.9711
3,000		.9251	.9421
4,000		.9044	.9159
5,000		.8874	.9004
6,000		.8716	.8845
7,000			.8703
8,000			.8583
9,000			.8475
10,000			.8373

The relative volumes are given in Table IX. The density at 0° at atmospheric pressure was taken as 0.8950, so that the volume decrements of the table are for this number of grams. The directly measured density at atmospheric pressure at 26.0° was 0.8768. In cal-

culating the density at 0°, the total expansion of one gram between 0° and 26° was taken to be 0.0234 cm³, as given by extrapolation of the sylphon readings.

Tri-caproin. $CH_3(CH_2)_4COOCH_2$
$CH_3(CH_2)_4COOCH$
$CH_3(CH_2)_4COOCH_2$
This was obtained from the Eastman Kodak Co. and used without further purification. The first run at 0° was to a maximum of 7500 kg, then at 50° to 11000, at 95° to 12000, and finally a check reading at 0° in perfect agreement. The average departure from a smooth curve of a single one of the 49 readings was 0.16%.

TABLE X.

RELATIVE VOLUMES OF TRI-CAPROIN.

Pressure kg/cm²	Temperature 0°	50°	95°
0	1.0000	1.0412	
500	.9741	1.0095	
1,000	.9547	.9850	1.0120
1,500	.9388	.9656	.9905
2,000	.9251	.9490	.9723
3,000	.9025	.9229	.9431
4,000	.8846	.9031	.9208
5,000	.8698	.8862	.9024
6,000	.8565	.8714	.8867
7,000	.8442	.8584	.8726
8,000	.8333	.8471	.8601
9,000		.8373	.8493
10,000		.8285	.8395
11,000		.8207	.8309
12,000			.8230

The relative volumes are given in Table X. The density at 0° at atmospheric pressure was taken to be 0.9970 so that the volume decrements of the table are for this number of grams. The measured density at atmospheric pressure at 27.0° was 0.9754. In computing the density at 0° the thermal expansion at atmospheric pressure of one gram between 0° and 50° was taken to be 0.0413 cm³, as given by extrapolation of the sylphon readings.

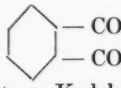
Normal-butyl Phthalate.  , $C_{16}H_{22}O_4$ This was obtained from the Eastman Kodak Co.; it had been specially freed from all volatile impurities so as to be ready for immediate use in diffusion pumps, and it was used directly in the sylphon with no attempt at further purification. A first attempt with this failed because of the development of a leak in the sylphon. The first set-up established, however, the safe pressure limits. The second set-up gave first a run at 0° to 8200 kg, then at 50° to 12000, at 95° to 12000, and then return check readings at both 0° and 95° again with good agreement. The average departure from smooth curves of a single one of the 48 readings was 0.16%.

TABLE XI.

RELATIVE VOLUMES OF NORMAL-BUTYL PHTHALATE.

Pressure	Temperature		
kg/cm²	0°	50°	95°
0	1.0000	1.0369	
500	.9768	1.0095	
1,000	.9575	.9872	1.0172
1,500	.9419	.9690	.9928
2,000	.9297	.9540	.9759
3,000	.9096	.9301	.9489
4,000	.8931	.9125	.9277
5,000	.8779	.8964	.9099
6,000	.8649	.8811	.8945
7,000	.8534	.8682	.8809
8,000	.8447	.8574	.8690
9,000		.8479	.8586
10,000		.8392	.8494
11,000		.8313	.8409
12,000		.8241	.8340

The relative volumes are given in Table XI. The density at 0° at atmospheric pressure was taken to be 1.0643, so that the volume decrements of the table are for this number of grams. The measured density at atmospheric pressure at 25.0° was 1.0453. In reducing this to the density at 0° the thermal expansion at atmospheric pressure of one gram between 0° and 25.0° was taken to be 0.0173 cm³, as given by extrapolation of the sylphon readings.

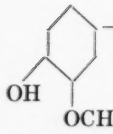
Eugenol.  , $C_{10}O_2H_{12}$ This material was obtained from the Eastman Kodak Co. and used without further purification. It was colorless in appearance, contrasted with the yellow color of the material which had been previously used in measurements of the viscosity under pressure.[4] As already mentioned, the compressibility of this was measured to give greater point to the measurements by W. E. Danforth, Jr., of the effect of pressure on dielectric constant, who in turn was interested in it because of the previously discovered enormously large increase of viscosity produced by pressure. For the purpose in mind, it was sufficient to determine the compressibility at a single temperature, 0°, because this was the temperature at which the interesting dielectric effects had been found. The maximum pressure at this temperature was only 4600 kg, this being as high as it was thought safe to go because of the greatly increased viscosity. As it was, the sylphon was damaged, the points with decreasing pressure lying off the curve, and the zero was greatly displaced. On opening the apparatus there was a distinct smell of eugenol, showing that the sylphon had leaked. This one run gave sufficient data for the purpose in hand, however, and no attempt was made to repeat the measurements. This run gave 8 points with increasing pressure, which lay remarkably well on a smooth curve, the average departure of a single reading being only 0.03% of the maximum effect.

TABLE XII.

RELATIVE VOLUMES OF EUGENOL.

Pressure kg/cm²	Temperature 0°
0	1.0000
500	.9801
1,000	.9639
1,500	.9501
2,000	.9382
3,000	.9187
4,000	.9028
5,000	.8896

The relative volumes are given in Table XII. The density at

atmospheric pressure at 25.9° was measured as 1.0515. No sylphon measurements were made from which the thermal expansion could be calculated, and there seem to be no values recorded in the literature. For the construction of the table the density at atmospheric pressure at 0° was assumed to be 1.065, using for the thermal expansion a mean from other organic compounds.

Iso-octane (2, 2, 4 tri-methyl pentane). This material I owe to the courtesy of Mr. A. E. Becker of the Standard Oil Development Co. The material had been refined in the research laboratory of this company in connection with experiments on motor fuels. They give for it the following physical constants. Boiling point: 99.3° within a range of 0.3°; specific gravity 0.6917 at 20° referred to water at 4°; freezing point — 107° C; aniline point 84°. It was used in the sylphon without further purification. A preliminary freezing point exploration indicated sharp freezing, evidence of high purity. Runs were made with a single filling of the apparatus, to 5600 kg at 0°, 8700 at 50°, 10200 at 95°, with a return check reading at 0° with very good agreement. The pressure limits of these runs were set by the preliminary freezing point examination. The average departure from smooth curves of a single one of the 40 readings was 0.075% of the maximum effect.

TABLE XIII.

RELATIVE VOLUMES OF ISO-OCTANE.

Pressure	Temperature		
kg/cm²	0°	50°	95°
0	1.0000	1.0607	
500	.9529	.9949	
1,000	.9221	.9560	.9851
1,500	.9001	.9286	.9531
2,000	.8825	.9077	.9292
3,000	.8558	.8764	.8946
4,000	.8356	.8529	.8684
5,000	.8161	.8318	.8453
6,000	.8037	.8176	.8307
7,000		.8038	.8161
8,000		.7911	.8024
9,000		.7797	.7901
10,000			.7795

The relative volumes are given in Table XIII. The density at 0° at atmospheric pressure was taken to be 0.7086, and the volume dec-

rements given in the table are for this number of grams. The directly measured density at atmospheric pressure was 0.6897 at 22.5°. In calculating the density at 0° the thermal expansion at atmospheric pressure between 0° and 22.5° was taken as 0.0385 cm³ per gm, obtained by extrapolation of the sylphon readings.

Isoprene. $CH_2 = C(CH_3) - CH = CH_2$ This material was synthesized at the Chemical Laboratory of Harvard University under the direction of Professor J. B. Conant. The effect of pressure in polymerizing this substance to a rubber-like material had already been extensively studied by Professor Conant[3], and it was of interest to determine the compressibility in connection with these studies. The material was used only a short time after it had been synthesized, and during this time as well as during the process of filling the sylphon it was maintained continuously at 0° in order to avoid danger of polymerization. The compressibility was attempted only at 0°, because at higher temperatures polymerization is known to proceed much more rapidly. No appreciable amount of polymerization was produced by the compressibility run, as shown by the agreement of the points obtained with increasing and decreasing pressure. The pressure range at 0° was safely taken to be the full 12000 kg, isoprene being a very volatile substance of low freezing point and low viscosity. The average departure from a smooth curve of a single one of the 18 readings was 0.16% of the maximum effect.

The relative volumes are given in Table XIV. The density at 0° at atmospheric pressure was taken to be 0.691. For this figure I am indebted to Dr. W. R. Peterson, who made a direct determination in the laboratory of Professor Conant.

Discussion.

This discussion will be mainly occupied with the attempt to correlate differences in the compressibility with differences in the structural formulas. It is worth mentioning, however, that certain general features of the p-v-t- relations of liquids already emphasized in two preceding papers[5] continue to hold for these liquids also. There is in the first place the reversal in the sign of $\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p$ at high pressures. At atmospheric and low pressures the sign of this is positive, but at pressures of the order of 3000 and over it had been found to become

TABLE XIV.

RELATIVE VOLUMES OF ISOPRENE.

Pressure kg/cm²	Temperature 0°
0	1.0000
500	.9524
1,000	.9208
1,500	.8973
2,000	.8781
3,000	.8478
4,000	.8252
5,000	.8070
6,000	.7911
7,000	.7776
8,000	.7658
9,000	.7551
10,000	.7450
11,000	.7357
12,000	.7272

negative, which means that at high pressures the thermal expansion of a liquid is less at high temperatures than at low temperatures at the same pressure. Inspection of the tables of volume of the new liquids of this paper will show that this continues to be true. A second general feature previously found was that $\left(\frac{\partial p}{\partial \tau}\right)_v$ is not a function of volume only, as had been assumed in various theoretical discussions by several authors. An application of the same method of analysis as that used in the preceding paper will show that for these new liquids also there are failures of the relation just as pronounced as found before.

Turning now to the relative behavior of the various compounds, the series terminating with glycerine is perhaps the most interesting. In Figure 1 are plotted the relative volume decrements at 50° of the five members of this series as a function of pressure, in terms of the respective volumes at 50° and atmospheric pressure as unity. 50° was chosen in order to allow comparison over a wider pressure range than would have been possible at 0°, where the range is often restricted by freezing. Included in the same diagram are the volumes of two of the alcohols and n-pentane for comparison. The most striking feature of the diagram is that the volume decrements of the four members of the series containing two OH groups in the molecule are very nearly alike.

The diagram also brings out in a very striking way that when an OH group is substituted into a hydrocarbon by far the most important factor in determining the compressibility is the number of OH's in

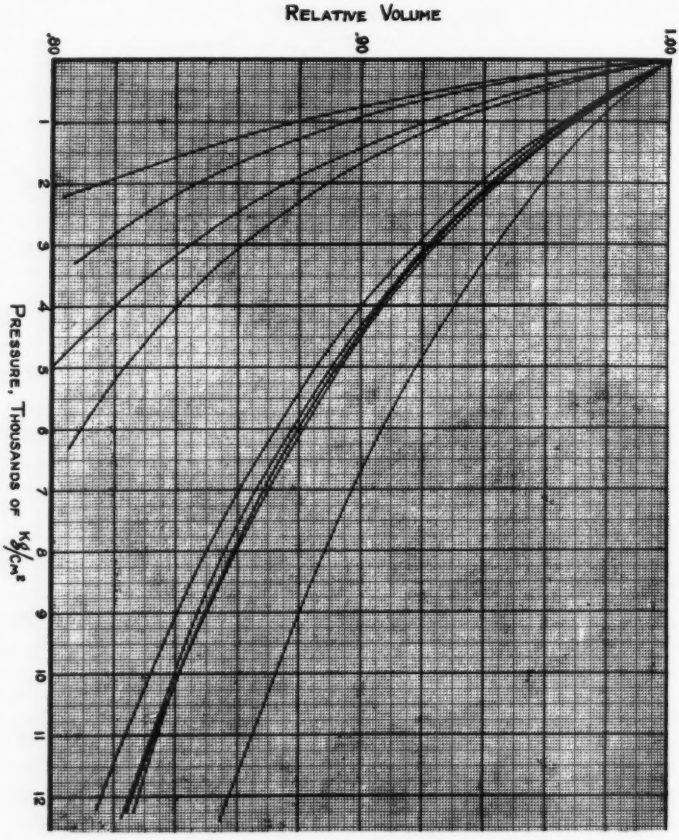


FIGURE 1. The relative volumes at 50° C of a number of liquids as a function of pressure. At 2000 kg/cm² the order of the curves, reading from the top down, is: glycerine, ethylene glycol, diethylene glycol, tri-methylene glycol, propylene glycol, amyl alcohol, methyl alcohol, n-hexane, and n-pentane.

the molecule, the compressibility decreasing as the number of OH's increases. This is shown in the diagram by the very marked tendency of the curves to fall into families, the unaltered hydrocarbons with no OH groups, typified by n-pentane, constituting the first family with the highest compressibility, the alcohols, which are hydrocarbon chains with one OH group, constituting the next family with lower compressibility, the four glycols of this paper with two OH groups, constituting the next family with still lower compressibility which is nearly the same for all members of the family, and finally glycerine, with three OH groups, and with the lowest compressibility of any organic liquid yet measured. It obviously suggests itself that in the search for organic compounds with low compressibility the natural course is to try those with a large number of OH groups in the molecule. Unfortunately, glycerine appears to be the last compound which is liquid under ordinary conditions, and even with it the liquidity is due only to its remarkable capacity for subcooling. It would be of interest, however, to study for its own sake the compressibility of solid compounds whose molecules contain more than three OH groups, for the same regularities which attach to the compressibility of the liquid phases will doubtless carry over to the solid phase. The study of solids is complicated, however, by the fact that for an exhaustive characterization of their behavior it will be necessary to measure the compressibility of single crystals in different directions.

Any detailed numerical study of the data presented in Figure 1 will encounter complications from temperature effects, the curves being in most cases drawn for the same temperature (50°) whereas doubtless a better method would have been to draw them for the same reduced temperature. This accounts for part of the effect of adding OH groups, for the addition of an OH group increases the critical temperature, so that 50° C becomes an increasingly smaller fraction of the critical temperature, and compressibility normally decreases on decreasing the reduced temperature. The same can be said for the behavior in a single family. On increasing the size of the molecule, keeping the number of OH groups constant, as, for example, in passing from methyl to amyl alcohol, the effect of increasing the length of the hydrocarbon chain is to raise the critical temperature. This is not by any means the entire effect, however, and the addition of the OH group does of itself markedly decrease the compressibility irrespective of the temperature effect, as shown, for example, by methyl alcohol and hexane, the critical temperature of the former being only 1% higher than that of the latter, while its compressibility is 16% less.

In seeking for an explanation of the effect of the OH group it is important to notice that the effect cannot be regarded as a specific contribution of the OH group only, without interaction with the rest of the molecule. If such were the case the compressibility of ethylene glycol [$C_2H_4(OH)_2$] should be practically the same as that of glycerine, the OH groups having .55 of the total mass of the molecule in the former compound, and .56 in the latter. Another example of the same sort is afforded by trimethylene and diethylene glycols. The OH groups constitute .46 of the weight of the molecule of the first and .32 of the second, yet the compressibilities are nearly the same. It is the number of OH groups in the molecule primarily rather than the fraction of the molecule occupied by OH groups which is determinative, although doubtless in very complicated compounds a single OH group may be swamped by the rest of the molecule. These facts suggest that in the molecule the OH groups interact with all the other parts of the molecule, consolidating them and decreasing the compressibility. Such effects are strongly suggested by wave mechanics.

A detailed comparison of the curves for the four glycols shows certain irregularities, of which the most prominent are the crossing of the ethylene and the diethylene glycol curves at 10000 kg, and the relatively large downward bulge in the trimethylene glycol curve between 6000 and 9000. Such irregularities are not at all unexpected in view of previous experience. A detailed explanation of them would be very complicated and doubtless beyond present day possibilities; I have suggested in a recent paper[6] that effects may be involved similar to the anomalies in the behavior of NH_4Cl and NH_4Br.

An interesting minor structural difference appears between propylene and trimethylene glycol, which differ only in the position of the OH groups; in the latter the two OH groups occupy the two ends of the chain, whereas in the former one OH occupies an end position and the other a mid position. The diagram shows that the propylene compound is distinctly more compressible.

Turning now to a comparison of the other substances, there are few structural similarities to suggest analogies of behavior. Of these, triacetin and tricaproin are the only ones with strictly similar structures. Both of these are in turn similar to glycerine, the difference being that in triacetin each OH group of glycerine is replaced by a CH_3COO group, and in tricaproin each OH group is replaced by a $CH_3(CH_2)_4COO$ group. One would expect similarities in the behavior

of these three substances. This, however, is not the case. In the first place both triacetin and tricaproin are much more compressible than glycerine, and in fact their compressibility is in excess of the compressibility of the glycols by a quantity of the same order of magnitude as that by which the compressibility of the glycols is in excess of that of glycerine. This again emphasizes the abnormally low compressibility of the OH group. Furthermore, triacetin is noticeably less compressible than tricaproin, the difference being of the order of 15%. This is not what might at first be expected, the usual rule being for the compressibility to decrease as one proceeds in a family of chemical compounds from those with small to those with larger and more complicated molecules. The evident significance of this abnormal behavior is that the compressibility of the $(CH_2)_4$ group is greater than the average compressibility of the CH_3COO group, an effect for which we are already prepared from our discussion of the glycerine family, where it was suggested that the compressibility of the hydrocarbon chain is rather high. In general, the presence of an O atom in a molecule seems to decrease the compressibility.

N-butyl phthalate and eugenol are similar in that they are substitution products of the benzene ring. In the former two H's of benzene have been replaced by two $COO(CH_2)_3\,CH_3$ groups, $C_{10}H_{18}O_4$ altogether, and in eugenol three H's have been replaced by CH_3O, OH, and $-CH_2-CH=CH_2$, or $C_4H_8O_2$ altogether. Because of the somewhat larger percentage of O in the eugenol replacement group, and particularly because of the presence of the OH group, one would expect the compressibility of eugenol to be less than that of the phthalate. This indeed proves to be the case, the compressibility of the latter being about 11% greater than that of the former. That the OH group does not impart a still more marked incompressibility is evidently explained by the fact that it is swamped by the rest of the molecule, which is much more complex in the ring compounds than in the members of the glycerine family.

Two other benzene substitution compounds have been previously investigated,[7] C_6H_5Cl and C_6H_5Br. These two compounds can be measured only over a small range because of freezing by pressure, but in the short range open to comparison the compressibilities of both are very nearly equal to that of the phthalate.

The structure of ethyl dibenzyl malonate is complicated and involves two benzene rings in the same molecule. It is liquid over only a small range of pressure; in this range its compressibility is very nearly the same as that of eugenol.

Tri-ortho-cresyl-phosphate contains three benzene rings, but there is a new element, phosphorus, so that we do not know exactly what to expect. As a matter of fact it is one of the more incompressible compounds, and is very close indeed to ethylene glycol. It would be interesting to examine phosphates containing OH groups if such exist.

Methyl oleate is essentially a long hydro-carbon chain with a $COOCH_3$ termination. The proportion of O atoms is small, so that one expects a compressibility of the same order as that of the higher straight hydro-carbons. The compressibility of the hydro-carbons has been measured as far out as n-decane. If the volume decrements at 0° produced by 1000 kg are plotted for these hydro-carbons as a function of the number of C's in the chain, and if due account is taken of the fact that the odd members of the family follow a different progression from the even members, the difference between odd and even vanishing asymptotically for long chains, it will be found that a natural and unforced extrapolation of the curve can be made from $n = 10$ (decane) to the volume decrement of methyl oleate at $n = 19$, 19 being the total number of C atoms in methyl oleate.

It is a curious fact that the volumes of methyl oleate and tricaproin are almost identical functions of pressure and temperature. This must be to a certain extent coincidence, the structure of the two being unlike.

Isoprene, C_5H_8, is essentially an iso-chain compound, with the number of H atoms cut down by the presence of two double bonds. The effect of a double bond seems to be in general to cut down the compressibility. One therefore expects a compressibility not greatly different from that of i-pentane, but somewhat less. This turns out to be the case, the volume decrement of isoprene at 0° at 7000 kg, for example, being about 10% less than that of i-pentane, and almost exactly the same as that of n-hexane.

The reason for measuring such an unusual compound as isoprene was, as already mentioned, that the data was of interest in connection with the work of Professor Conant on polymerization by pressure. The polymerization product has under normal conditions a volume of the order of 20% less than isoprene, so that it is at first natural to think that the polymerization is a pure pressure effect connected with the change of volume. The rate of polymerization increases rapidly with increasing pressure, however, and at the same time the volume of isoprene approaches that of the polymerization product, because of the very much greater compressibility of isoprene, now established by

these measurements. In fact, special experiments in which the polymerization was conducted at 20000 kg showed that at this pressure the rate is more rapid than at any lower pressure, but that the change of volume is not perceptible. It is therefore evident that some other effect than that of pure volume change must be responsible for the polymerization. The situation has been studied in full detail, and a solution proposed, in papers by Professor Conant.[3]

Finally, the measurements on i-octane must be mentioned. One would expect a compressibility very nearly the same as that of n-octane, but somewhat less, judging from the effect of the iso-structure as shown by the behavior of n- and i- pentane, for example. This turns out to be the case, the volume decrement at 0° and 5000 kg, for example, of i-octane, being 0.9% less than that of n-octane.

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THE JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY, CAMBRIDGE, MASS.

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